

What is claimed is:

1. A method for preparing a photoresist composition, comprising:
 - a) providing a polymer by a polymerization reaction that comprises adding over the substantial course of the polymerization reaction one or more incorporated polymerization reagents to a reaction mixture; and
 - b) admixing the polymer with a photoactive component.
2. The method of claim 1 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the fastest reaction rate relative to the other incorporated polymerization reagents is added to the reaction mixture over the substantial course of the polymerization reaction.
3. The method of claim 1 or 2 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the second fastest reaction rate relative to the other incorporated polymerization reagents is added to the reaction mixture over the substantial course of the polymerization reaction.
4. The method of any one of claims 1 through 3 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the slowest fastest reaction rate relative to the other incorporated polymerization reagents is present in the reaction mixture at the start of the polymerization reaction and is not added to the reaction mixture over the substantial course of the polymerization reaction.
5. The method of any one of claims 1 through 4 wherein maleic anhydride is added to the reaction mixture over the substantial course of the polymerization reaction.

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6. The method of any one of claims 1 through 5 wherein an acrylate compound is added to the reaction mixture over the substantial course of the polymerization reaction.

7. The method of claim 6 wherein the acrylate compound comprises a photoacid-labile ester.

8. The method of any one or claims 1 through 7 wherein a reaction mixture that contains one or more polymerization reagents is initially provided at the start of the polymerization reaction, and

one or more additional polymerization reagents are added to the reaction mixture over the substantial course of the polymerization reaction.

9. The method of claim 8 wherein the reaction mixtures comprises an optionally substituted carbon alicyclic compound or an optionally substituted heteroalicyclic compound at the start of the polymerization reaction.

10. The method of claim 8 wherein the reaction mixtures comprises an optionally substituted norbornene compound or an optionally substituted oxygen heteroalicyclic compound at the start of the polymerization reaction.

11. The method of claim 1-3 or 5-7 wherein each polymerization reagent is added to a reaction mixture over the substantial course of the polymerization reaction.

12. The method of any one of claims 1 through 11 wherein the polymerization reaction is a free radical mediated reaction.

13. The method of any one of claims 1 through 11 wherein the polymerization reaction is an anionic, cationic or metal catalyzed reaction.

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14. The method of any one of claims 1 through 13 wherein one or more of the polymerization reagents is selected from the group consisting of an anhydride, a lactone, a fluorinated olefin, a carbon alicyclic compound, a heteroalicyclic compound, or an acrylate.

15. The method of any one of claims 1 through 13 wherein one or more of the polymerization reagents is 2-methyladamantanyl methacrylate, 2-methyladamantanyl acrylate, maleic anhydride, norbornene, 3,4-dihydropyran, or tetrafluoroethylene.

16. The method of any one of claims 1 through 15 wherein each of the polymerization reagents is a non-aromatic compound.

17. The method of any one of claims 1 through 15 wherein one or more of the polymerization reagents is an aromatic compound.

18. The method of any one of claims 1 through 15 wherein one or more of the polymerization reagents comprises an optionally substituted phenyl or optionally substituted naphthyl moiety.

19. The method of any one of claims 1 through 18 wherein one or more polymerization reagents are added over at least about 80 percent of the duration of the polymerization reaction.

20. The method of any one of claims 1 through 19 wherein at least two polymerization reagents are added over the substantial course of the polymerization reaction.

21. The method of any one of claims 1 through 20 wherein a radical initiator compound is added over the substantial course of the polymerization reaction.

22. The method of claim 21 wherein the initiator is added at a rate to maintain a substantially constant concentration of initiator within the reaction mixture over the substantial course of the polymerization reaction.

23. The method of any one of claims 1 through 22 wherein a reaction vessel is initially charged with one or more polymerization reagents, and one or more polymerization reagents having a faster reaction rate than the charged reagents are added to the reaction vessel over the substantial course of the polymerization reaction.

24. The method of any one of claims 1 through 23 wherein a fluorinated olefin, an anhydride or a lactone is added over the substantial course of the polymerization reaction.

25. The method of any one of claims 1 through 23 wherein an acrylate compound and maleic anhydride are added over the substantial course of a reaction to a reaction mixture comprising an optionally substituted norbornene compound.

26. The method of any one of claims 1 through 23 wherein an acrylate compound and maleic anhydride are added over the substantial course of a reaction to a reaction mixture comprising an optionally substituted norbornene compound and an optionally substituted dihydropyran.

27. The method of any one of claims 1 through 26 wherein at least one of the polymerization reagents is added at a rate decreasing over the substantial course of the polymerization reaction.

28. The method of any one of claims 1-3, 5-10 or 12-27 wherein the one or more polymerization reagents are contained in a reaction vessel and one or more polymerization reagents are added to the reaction vessel over the substantial course of the polymerization reaction.

29. The method of any one of claims 1 through 28 wherein the photoactive component comprises one or more photoacid generator compounds.

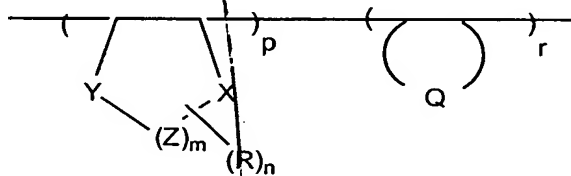
30. The method of any one of claims 1 through 29 wherein the polymer comprises photoacid labile repeat units that contain a tertiary alicyclic group.

31. The method of any one of claims 1 through 30 wherein the polymer comprises a polymerized fluorinated unsaturated monomer.

32. The method of any one of claims 1 through 31 wherein the polymer comprises a fused heteroalicyclic.

33. The method of any one of claims 1 through 32 wherein the polymer comprises a fused heteroalicyclic group having an oxygen ring member.

34. The method of any one of claims 1 through 33 wherein the polymer comprises a structure of the following formula:

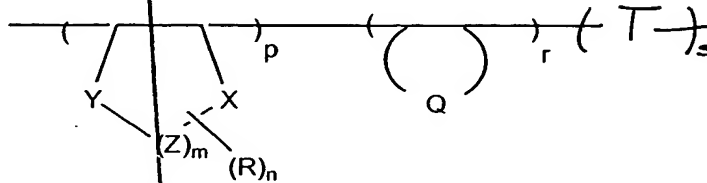


wherein X, Y and Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur, and preferably no more than two of X, Y and Z being oxygen or sulfur;

Q represents an optionally substituted carbon alicyclic group fused to the polymer backbone;

p and r are the mole fractions of the respective units and each of p and r is greater than zero.

35. The method of any one of claims 1 through 33 wherein the polymer comprises a structure of the following formula:



wherein T is an optionally substituted acrylate group;

X, Y and Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur, and preferably no more than two of X, Y and Z being oxygen or sulfur;

Q represents an optionally substituted carbon alicyclic group fused to the polymer backbone;

p, r and s are the mole fractions of the respective units and each of p, r and s is greater than zero.

36. The method of claim 35 wherein T comprises a photoacid-labile moiety.

37. The method of any one of claims 1 through 36 wherein the composition is a chemically-amplified positive-acting resist.

38. The method of any one of claims 1 through 36 wherein the composition is a negative-acting resist.

39. The method of any one of claims 1 through 38 further comprising applying a coating layer of the photoresist composition on a substrate; exposing the

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photoresist coating layer to patterned activating radiation; and developing the exposed photoresist coating layer to provide a resist relief image.

40. The method of claim 39 wherein the photoresist layer is exposed with radiation having a wavelength of less than about 300 nm.

41. The method of claim 39 wherein the photoresist layer is exposed with radiation having a wavelength of less than about 200 nm.

42. The method of claim 39 wherein the photoresist layer is exposed with radiation having a wavelength of about 193 nm.

43. The method of ~~any~~ one of claims 39 through 42 wherein the substrate is a microelectronic wafer.

44. A photoresist composition comprising a photoactive component and a polymer obtainable by adding over the substantial course of a polymerization reaction one or more polymerization reagents to a reaction mixture.

45. A photoresist composition of claim 44 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the fastest reaction rate relative to the other incorporated polymerization reagents is added to the reaction mixture over the substantial course of the polymerization reaction.

46. A photoresist composition of claim 44 or 45 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the second fastest reaction rate relative to the other incorporated polymerization reagents is added to the reaction mixture over the substantial course of the polymerization reaction.

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47. A photoresist composition of any one of claims 44 through 46 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the slowest fastest reaction rate relative to the other incorporated polymerization reagents is present in the reaction mixture at the start of the polymerization reaction and is not added to the reaction mixture over the substantial course of the polymerization reaction.

48. A photoresist composition of any one of claims 44 through 47 wherein maleic anhydride is added to the reaction mixture over the substantial course of the polymerization reaction.

49. A photoresist composition of any one of claims 44 through 47 wherein an acrylate compound is added to the reaction mixture over the substantial course of the polymerization reaction.

50. A photoresist composition of claim 49 wherein the acrylate compound comprises a photoacid-labile ester.

51. A photoresist composition of any one or claims 44 through 50 wherein a reaction mixture that contains one or more polymerization reagents is initially provided at the start of the polymerization reaction, and
one or more additional polymerization reagents are added to the reaction mixture over the substantial course of the polymerization reaction.

52. A photoresist composition of claim 51 wherein the reaction mixtures comprises an optionally substituted carbon alicyclic compound or an optionally substituted heteroalicyclic compound at the start of the polymerization reaction.

53. A photoresist composition of claim 51 wherein the reaction mixtures comprises an optionally substituted norbornene compound or an optionally substituted oxygen heteroalicyclic compound at the start of the polymerization reaction.

54. A photoresist composition of claim 44-46 or 48-53 wherein each polymerization reagent is added to a reaction mixture over the substantial course of the polymerization reaction.

55. A photoresist composition of any one of claims 44 through 54 wherein the polymerization reaction is a free radical mediated reaction.

56. A photoresist composition of any one of claims 44 through 55 wherein the polymerization reaction is an anionic, cationic or metal catalyzed reaction.

57. A photoresist composition of any one of claims 44 through 56 wherein one or more of the polymerization reagents is selected from the group consisting of an anhydride, a lactone, a fluorinated olefin, a carbon alicyclic compound, a heteroalicyclic compound, or an acrylate.

58. A photoresist composition of any one of claims 44 through 56 wherein one or more of the polymerization reagents is 2-methyladamantanyl methacrylate, 2-methyladamantanyl acrylate, maleic anhydride, norbornene, 3,4-dihydropyran, or tetrafluoroethylene.

59. A photoresist composition of any one of claims 44-46, 48-53 or 55-58 wherein each of the polymerization reagents is a non-aromatic compound.

60. A photoresist composition of any one of claims 44 through 58 wherein one or more of the polymerization reagents is an aromatic compound.

61. A photoresist composition of any one of claims 44 through 58 wherein one or more of the polymerization reagents comprises an optionally substituted phenyl or optionally substituted naphthyl moiety.

62. A photoresist composition of any one of claims 44 through 61 wherein one or more polymerization reagents are added over at least about 80 percent of the duration of the polymerization reaction.

63. A photoresist composition of any one of claims 44 though 61 wherein at least two polymerization reagents are added over the substantial course of the polymerization reaction.

64. A photoresist composition of any one of claims 44 through 62 wherein a radical initiator compound is added over the substantial course of the polymerization reaction.

65. A photoresist composition of claim 64 wherein the initiator is added at a rate to maintain a substantially constant concentration of initiator within the reaction mixture over the substantial course of the polymerization reaction.

66. A photoresist composition of any one of claims 44 through 65 wherein a reaction vessel is initially charged with one or more polymerization reagents, and one or more polymerization reagents having a faster reaction rate than the charged reagents are added to the reaction vessel over the substantial course of the polymerization reaction.

67. A photoresist composition of any one of claims 44 through 66 wherein a fluorinated olefin, an anhydride or a lactone is added over the substantial course of the polymerization reaction.

68. A photoresist composition of any one of claims 44 through 67 wherein an acrylate compound and maleic anhydride are added over the substantial course of a reaction to a reaction mixture comprising an optionally substituted norbornene compound.

69. A photoresist composition of any one of claims 44 through 68 wherein an acrylate compound and maleic anhydride are added over the substantial course of a reaction to a reaction mixture comprising an optionally substituted norbornene compound and an optionally substituted dihydropyran.

70. A photoresist composition of any one of claims 44 through 69 wherein at least one of the polymerization reagents is added at a rate decreasing over the substantial course of the polymerization reaction.

71. A photoresist composition of any one of claims 44-58 or 60-70 wherein the one or more polymerization reagents are contained in a reaction vessel and one or more polymerization reagents are added to the reaction vessel over the substantial course of the polymerization reaction.

72. A photoresist composition of any one of claims 44 through 71 wherein the photoactive component comprises one or more photoacid generator compounds.

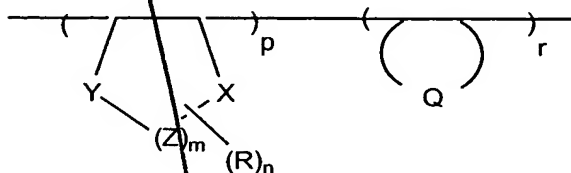
73. A photoresist composition of any one of claims 44 through 72 wherein the polymer comprises photoacid labile repeat units that contain a tertiary alicyclic group.

74. A photoresist composition of any one of claims 44 through 73 wherein the polymer comprises a polymerized fluorinated unsaturated monomer.

75. A photoresist composition of any one of claims 44 through 74 wherein the polymer comprises a fused heteroalicyclic.

76. A photoresist composition of any one of claims 44 through 75 wherein the polymer comprises a fused heteroalicyclic group having an oxygen ring member.

77. A photoresist composition of any one of claims 44 through 76 wherein the polymer comprises a structure of the following formula:

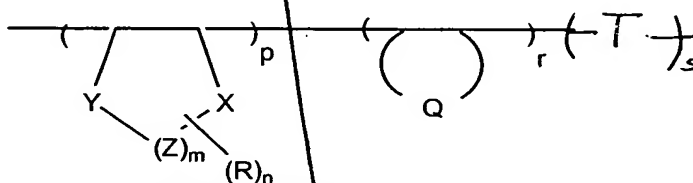


wherein X, Y and Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur, and preferably no more than two of X, Y and Z being oxygen or sulfur;

Q represents an optionally substituted carbon alicyclic group fused to the polymer backbone;

p and r are the mole fractions of the respective units and each of p and r is greater than zero.

78. The photoresist composition of any one of claims 44 through 76 wherein the polymer comprises a structure of the following formula:



wherein T is an optionally substituted acrylate group;

X, Y and Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur, and preferably no more than two of X, Y and Z being oxygen or sulfur;

Q represents an optionally substituted carbon alicyclic group fused to the polymer backbone;

p, r and s are the mole fractions of the respective units and each of p, r and s is greater than zero.

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79. A photoresist composition of claim 78 wherein T comprises a photoacid-labile moiety.

80. A photoresist composition of any one of claims 44 through 79 wherein the composition is a chemically-amplified positive-acting resist.

81. A photoresist composition of any one of claims 44 through 79 wherein the composition is a negative-acting resist.

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82. A method of forming a photoresist relief image, comprising:
(a) applying a coating layer of a photoresist of any one of claims 44 through 81 on a substrate; and
(b) exposing and developing the photoresist layer to yield a relief image.

83. The method of claim 82 wherein the photoresist layer is exposed with radiation having a wavelength of less than about 300 nm.

84. The method of claim 82 wherein the photoresist layer is exposed with radiation having a wavelength of less than about 200 nm.

85. The method of claim 82 wherein the photoresist layer is exposed with radiation having a wavelength of about 193 nm.

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86. An article of manufacture comprising a microelectronic wafer substrate or flat panel display substrate having coated thereon a layer of the photoresist composition of any one of claims 44 through 81.

87. A method for preparation of a photoresist composition comprising:

providing a polymer obtainable by adding over the substantial course of a polymerization reaction one or more polymerization reagents to a reaction mixture; and

admixing the polymer with a photoactive component.

88. A method for producing a polymer comprising adding over the substantial course of a polymerization reaction one or more polymerization reagents to a reaction mixture.

89. The method of claim 88 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the fastest reaction rate relative to the other incorporated polymerization reagents is added to the reaction mixture over the substantial course of the polymerization reaction.

90. The method of claim 88 or 89 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the second fastest reaction rate relative to the other incorporated polymerization reagents is added to the reaction mixture over the substantial course of the polymerization reaction.

91. The method of any one of claims 88 through 90 wherein multiple incorporated polymerization reagents are reacted, and the incorporated polymerization reagent with the slowest fastest reaction rate relative to the other incorporated polymerization reagents is present in the reaction mixture at the start of the polymerization reaction and is not added to the reaction mixture over the substantial course of the polymerization reaction.

92. The method of any one of claims 88 through 91 wherein maleic anhydride is added to the reaction mixture over the substantial course of the polymerization reaction.

93. The method of any one of claims 88 through 92 wherein an acrylate compound is added to the reaction mixture over the substantial course of the polymerization reaction.

94. The method of claim 93 wherein the acrylate compound comprises a photoacid-labile ester.

95. The method of any one of claims 88 through 94 wherein a reaction mixture that contains one or more polymerization reagents is initially provided at the start of the polymerization reaction, and

one or more additional polymerization reagents are added to the reaction mixture over the substantial course of the polymerization reaction.

96. The method of claim 95 wherein the reaction mixtures comprises an optionally substituted carbon alicyclic compound or an optionally substituted heteroalicyclic compound at the start of the polymerization reaction.

97. The method of claim 95 wherein the reaction mixtures comprises an optionally substituted norbornene compound or an optionally substituted oxygen heteroalicyclic compound at the start of the polymerization reaction.

98. The method of any one of claims 87-90, 92-94 or 96-97 wherein each polymerization reagent is added to a reaction mixture over the substantial course of the polymerization reaction.

99. The method of any one of claims 88 through 98 wherein the polymerization reaction is a free radical mediated reaction.

100. The method of any one of claims 88 through 98 wherein the polymerization reaction is an anionic, cationic or metal catalyzed reaction.

101. The method of any one of claims 88 through 100 wherein one or more of the polymerization reagents is selected from the group consisting of an anhydride, a lactone, a fluorinated olefin, a carbon alicyclic compound, a heteroalicyclic compound, or an acrylate.

102. The method of any one of claims 88 through 101 wherein one or more of the polymerization reagents is 2-methyladamantanyl methacrylate, 2-methyladamantanyl acrylate, maleic anhydride, norbornene, 3,4-dihydropyran, or tetrafluoroethylene.

103. The method of any one of claims 88 through 102 wherein each of the polymerization reagents is a non-aromatic compound.

104. The method of any one of claims 88 through 102 wherein one or more of the polymerization reagents is an aromatic compound.

105. The method of any one of claims 88 through 104 wherein one or more of the polymerization reagents comprises an optionally substituted phenyl or optionally substituted naphthyl moiety.

106. The method of any one of claims 88 through 105 wherein one or more polymerization reagents are added over at least about 80 percent of the duration of the polymerization reaction.

107. The method of any one of claims 88 through 106 wherein at least two polymerization reagents are added over the substantial course of the polymerization reaction.

108. The method of any one of claims 88 through 107 wherein a radical initiator compound is added over the substantial course of the polymerization reaction.

109. The method of claim 108 wherein the initiator is added at a rate to maintain a substantially constant concentration of initiator within the reaction mixture over the substantial course of the polymerization reaction.

110. The method of any one of claims 88-97 or 99-109 wherein a reaction vessel is initially charged with one or more polymerization reagents, and one or more polymerization reagents having a faster reaction rate than the charged reagents are added to the reaction vessel over the substantial course of the polymerization reaction.

111. The method of any one of claims 88 through 110 wherein a fluorinated olefin, an anhydride or a lactone is added over the substantial course of the polymerization reaction.

112. The method of any one of claims 88 through 111 wherein an acrylate compound and maleic anhydride are added over the substantial course of a reaction to a reaction mixture comprising an optionally substituted norbornene compound.

113. The method of any one of claims 88 through 111 wherein an acrylate compound and maleic anhydride are added over the substantial course of a reaction to a reaction mixture comprising an optionally substituted norbornene compound and an optionally substituted dihydropyran.

114. The method of any one of claims 88 through 113 wherein at least one of the polymerization reagents is added at a rate decreasing over the substantial course of the polymerization reaction.

115. The method of any one of claims 88 through 113 wherein the one or more polymerization reagents are contained in a reaction vessel and one or more polymerization reagents are added to the reaction vessel over the substantial course of the polymerization reaction.

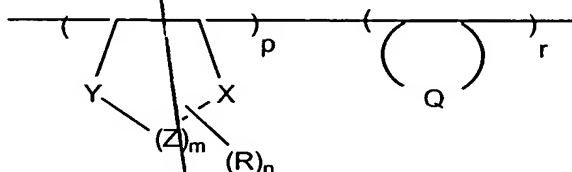
116. The method of any one of claims 88 through 115 wherein the polymer comprises photoacid labile repeat units that contain a tertiary alicyclic group.

117. The method of any one of claims 88 through 116 wherein the polymer comprises a polymerized fluorinated unsaturated monomer.

118. The method of any one of claims 88 through 117 wherein the polymer comprises a fused heteroalicyclic.

119. The method of any one of claims 88 through 118 wherein the polymer comprises a fused heteroalicyclic group having an oxygen ring member.

120. The method of any one of claims 88 through 119 wherein the polymer comprises a structure of the following formula:

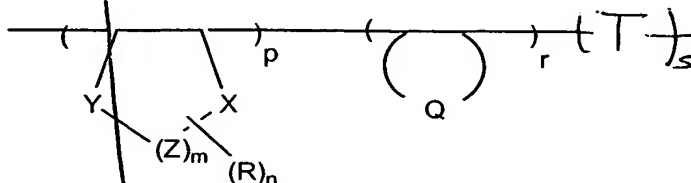


wherein X, Y and Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur, and preferably no more than two of X, Y and Z being oxygen or sulfur;

Q represents an optionally substituted carbon alicyclic group fused to the polymer backbone;

p and r are the mole fractions of the respective units and each of p and r is greater than zero.

121. The method composition of any one of claims 88 through 119 wherein the polymer comprises a structure of the following formula:



wherein T is an optionally substituted acrylate group;

X, Y and Z are each independently carbon, oxygen or sulfur, with at least one of X, Y or Z being oxygen or sulfur, and preferably no more than two of X, Y and Z being oxygen or sulfur;

Q represents an optionally substituted carbon alicyclic group fused to the polymer backbone;

p, r and s are the mole fractions of the respective units and each of p, r and s is greater than zero.

122. The method of claim 121 wherein T comprises a photoacid-labile moiety.

123. A polymer obtained by a method of any one of claims 88 through 122.

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